Translated from the German

European Patent Office

EUROPEAN PATENT SPECIFICATION
EP 0 545 043 B1

IPC: D21H 11/14, G03C 1/775

(45) Date of making available to the public by printing of the B1 patent document, on which grant has taken place on or before the said date: August 23, 1995
(22) Date of application: October 14, 1992

---

(54) Title in German of the object of the invention: Basispapier für fotografische Schichtträger

---

(30) Priority data: November 29, 1991 DE 41 39 251
(43) Date of making available to the public of the patent application, on which no grant has taken place on or before the said date: June 9, 1993 in *Patentblatt* 93/23
(45) Making available to the public the Notice about the granting of the patent: August 23, 1995 in Patentblatt 95/34
(84) Designated high contracting parties to regional patent conventions:
AT BE CH DE DK ES FR GB IE IT LI LU NL PT SE
(56) Prior art documents/citations:
EP-A- 0 362 823
DE-A- 3 044 781
US-A- 4,994,147
Dialog Information Services, File 240 PA-PERCHEM, A. N. 63-06180;
Hongo et al. "Paper for electrophotographic copying" JP-A-3220398 (September 27, 1991)
Journal of Applied Photographic Engineering, vol. 7, No. 4, August 1981, Rochester, US, pp 117 - 120, Woodward "The Evolution of Photographic Basepapers".
(73) Patent Owner: Felix Schwelle, Jr. Papierfabrik GmbH & Co. KG, D-49086 Osnabrück

(72) Inventors: Alois Kerkhoff et al.
(74) Attorneys: Minderop & Florack, Patent attorneys, D-40435 Düsseldorf

* = Translator's notes

BASE PAPER FOR PHOTOGRAPHIC SUPPORTS

Description

As raw (base) paper* [*a.k.a. body stock] for the manufacturing of photographic emulsion carriers (a.k.a supports), there is made a wet-strength, dimensionally stable paper, which must be free of photochemical and mechanical impurities or contaminants. The sizing of the paper must always be so aligned that it counteracts the swelling effect when aqueous aftertreatment takes place.

A resin coating prevents the penetration of chemicals and water into the base (raw) paper over the course of the development. Hence, until recently, only special pulps (chemical pulps), so-called photographic celluloses or photographic chemical pulps were used as fibrous materials for the base paper, which photographic celluloses has a particular degree or percentage of purity. In doing so, the point under consideration pertains to bleached sulfite- or sulfate-celluloses from coniferous and deciduous trees. The bleaching method, which - generally speaking

– is used for these types of cellulose, is the chlorine-bleaching method, having a deleterious impact upon the environment. In the recent years, a technological conversion is taking place - in the area of the bleaches - to "environmentally friendly or ecologically sound" bleaching agent. Thus, in the Japanese A1 patent document JP-A-63-303 191, there is described a photographic emulsion carrier (support), for whose manufacturing an oxygen-bleached pulp is used.

The endeavors to conserve the raw materials' sources, and to use environmentally friendly manufacturing process should also be extended to other areas.

Hence, it is an object of the invention to propose a base paper for photographic emulsion carriers, which not only satisfies all conventional requirements for photographic base paper, such as, e.g., glaze, a surface after the processing in photographic baths, inflexibility, plybond strength (internal bond strength), photochemical neutrality with respect to light-sensitive emulsions, but also the requirement for a better raw-materials utilization and an environmentally friendly production design, which requirement is prevalent among the public due to ecological reasons.

The set objective is achieved as a result of the fact that for the manufacturing of the base paper, there is used a fibrous material, which contains between 5 and

100% of recycled paper stock.

The base paper can also completely consist of recycled paper stock, but also of a mixture of recycled paper stock with standard cellulose or photographic cellulose.

The term recycled paper denotes a paper stock, which is generated of scrap (waste) paper by menas of suitable and known stock preparation (fiber preparation) methods.

The scrap paper thus used are classified and characterized according to kind or sort groups as well as within the sort-groups (Waste-paper List of the German Standard Sorts and their Quality, Union of the German Paper Manufacturers, valid from 1/1/1989).

In a separate embodiment of the invention, the paper core can also contain a photographic cellulose and/or standard cellulose.

The term photographic celluloses implies a cellulose, which has been qualified for the photographic-paper manufacturers with regard to its mechanical and photochemical impurities or contaminants, i.e. that the content of dirt particles (contaminating) particles may not exceed 1.7 mm2/m2, and the content of the iron- and copper-contaminants, which are deleterious for the photographic emulsions may not exceed 30 points/kg of chemical pulp.

The paper core can be sized (neutral sizing) by using dimerized alkyl chains in the neutral pH-range together with cationic resins, such as, e.g., cationic polyamide-polyamine-epichlorohydrin resin, cationic polyacrylamides, cationic starches, or polyethylene imines. Alkyl-chain dimers, having alkyl chains of different length, are used. A particularly preferred dimerized alkyl chain consists at least of 50% of behenyl chains or another alkyl chain, having more than 18 atoms in the alkyl group. The hydrocarbon group of the chains can also contain ring-structures or C=C-double bonds.

For the neutral sizing, there can also be used other reactive sizing or bonding agents, such as, e.g., epoxidized fatty acid amides, fatty acid anhydrides, or an alkyl succinic anhydride.

In another embodiment form of the invention, the paper core is sized (acid sizing) by using non-reactive sizing agents, such as higher fatty acids or fatty-acid salts in an acid pH-range from 3.5 to 5 together with polyvalent metal ions in the form of a salt, such as aluminum sulfate, anhydrous aluminum chloride, or sodium aluminate. The fatty acids can be saturated or unsaturated. They contain 14 to 20 C-atoms, and are, e.g., palmitic acid, stearic acid, or oleic acid. Preferred is stearic acid, as well as its salts, e.g., sodium stearate.

In other embodiment forms of the invention, two or more hydrophobic or

water-repellent sizing agents are contained in the paper. In doing so, reactive sizing agents can be combined with non-reactive sizing agents. For example, a preferred combination is a combination of alkyl chains dimers and fatty acids, but also a combination of an epoxidized fatty-acid amide and fatty acid is possible within the framework of the invention.

Base papers, made in accordance with the invention can contain all otherwise conventional additives or admixtures such as white pigments, colorants, coloring pigments, fillers, and other auxiliary agents.

In another embodiment form of the invention, the paper core - besides being provided with an inner sizing - is additionally provided with a surface-sizing, which, e.g., consists of a starch-coating or polyvinyl-alcohol coating, which is applied as aqueous solution upon the paper web with the help of a known method of application. The applied amount constitutes 0.5 to 10 g/m^2, preferably 1 to 4.5 g/m^2.

The paper core in accordance with the invention can then be coated at least on one side with a synthetic-resin layer.

In a separate embodiment of the invention, the paper core in accordance with the invention is coated with a synthetic-resin layer, which is cured as a result of being subjected to UV-irradiation, or electron-beam irradiation, respectively. The

coating, which has been solidified by means of irradiation, preferably contains pigment - besides the bonding agent - and has a basis weight* [*a.k.a. gram weight] 5 to 40 g/m^2. The bonding agent essentially consists of such substances, which contain C-C-double bonds. Preferred pigments are white pigments, such as TiO_2, $BaSO_4$, ZnO, $CaCO_3$, and also coloring pigments.

The synthetic-resin layer, which has been applied at least on one side upon the paper core, can also be applied in aqueous dispersion. Natural or synthetic polymer compounds can be used as bonding agents. In addition to the bonding agent, the layer can yet contain other additives, such as white pigments, colorant, hardening agents, and similar.

The paper core in accordance with the invention can also be provided at least on one side with a synthetic-resin layer, which is applied by mans of extrusion coating. The thermoplastic resins, used to this end, are preferably polyolefins, in particular polyethylenes (HDPE, LDPE), ethylene/α-olefin copolymers (LDPE), or polypropylene. The polypropylene coating can contain a light-reflecting white pigment, such as, e.g., coloring pigments, optical fluorescent whitening agents, antistatic agents (static eliminators), deflocculating agents, and other additives. The amount of the coating, which is applied constitutes 5 to 50 g/m^2. Preferred pigments are titanium oxides of rutile or anatase (native titanium

dioxide) type, which are introduced in an amount of 5 to 20 % by weight.

Surprisingly enough, it turned out that photographic base papers, made by using of recycled paper stock, can be compared - as far as the required properties are concerned, such as, e.g., surface quality, edge penetration of photographic liquids, or photochemical neutrality - to photographic base papers, made by using photographic celluloses.

The invention is elucidated by means of the following examples.

Besides the various types of waste paper, described in Example 1, there were examined other kinds of waste paper for the recycled paper stock, and were found that they can be used.

Example 1

A fibrous material mixture, corresponding to that in Table 1, was - at a stock (pulp) consistency of 4% - beaten to a freeness value of 35° SR. Neutral sizing agents

(high density pulp: 2.5 % of TiO_2, 0.057 % of fluorescent bleaching agent, 1.5% of anionic starch
low density pulp: 0.7 polyamide/polyamine-epichlorohydrin resin,
0.5% of alkyl chain dimer,
0.11 % of epoxidized fatty acid amide)

were then added to the fibrous material suspension, and out of 1.2% by weight of diluted suspension, there were made - in the known way - approximately 170 g/m^2

of a heavy base paper. The papers - also in a known way – were surface-sized with the help of a solution, which contained 4.4% by weight of oxidized starch, 0.03% of fluorescent bleaching agent, and 21 g/l of NaCl.

Table 1 on the next page

Table 1

Composition of the fibrous material mixture in % by weight						
Kind of fibrous material	1.1	1.2	1.3	1.4	1.5	1.6
Deci-duos-tree sulfate cellulose (photo-graphic cellu-lose) ---------- Deci-duos-tree sulfate cellulose (stan-dard)	70	70	70	70	70	30 40
Recycled paper stock						
a	30					
b		30				
c			30			
d				30	30	30
a:	cellulose wrappers (own waste)					

b:	own wastes + office paper (sort 19)
c:	wood-free sorting products (sort R12), and wood-free, white office paper
d:	multi-print (wood-free, printed, printed, waste paper (sort K22)

Example 2

In a way, analogous to Example 1, there were produced about 170 g/m^{2}of heavy paper stock.

The composition of the fibrous material mixture is sited in Table 2.

Table 2

Composition of the fibrous material mixture in % by weight			
Kind of fibrous material	2.1	2.2	2.3
Deciduos-tree sulfate cellulose (photographic cellulose)	90	50	-
Recycled paper stock *d*	10	50	100

Example 3:

A mixture of 30% by weight of recycled paper stock of sort F and 70% by weight of deciduous-tree sulfate cellulose was - at a stock consistency of 4 % -

beaten to a freeness value of 35° SR. To the pulp suspension, there were added then surface-sizing agents (high density pulp: 0.04% by weight of fluorescent bleaching agent, 0.35% by weight of anionic polyacrylamide, 1.55% by weight of stearin, 0.8% by weight of alum, 0.54 % by weight of cationic polyacrylamide; low-density pulp: 0.41% by weight of polyamide/polyamine-epichlorohydrin resin) at a hydrogen-ion concentration, pH = 4.5. Out of the suspension, diluted approximately to about 1.2% by weight, approximately 170 g/m^{2}of a heavy base paper stock was made in known way. The paper was in likewise known way surface-sized with a solution, which contained 3.45% by weight of polyvinyl alcohol, 4% by weight of $CaCl_2$ x $2H_2O$ and 0.53% by weight of fluorescent bleaching agent.

Comparative Example 1

A mixture of 100% by weight of deciduous-tree sulfate cellulose (photographic cellulose) was beaten - at a stock (pulp) consistency of 4% - to a freeness value of 35° SR. Neutral sizing agents, as cited in example 1, were then added to the pulp suspension, and approximately 170 g/m^2 of a heavy base paper stock were produced in known way.

In a way, analogous to that cited in Example 1, the papers were surface-sized.

Comparative Example 2

To a cellulose suspension, in accordance with Comparative Example 1, there were added sizing agents, as in Example 3, and approximately 170 g/m^2 of a heavy base paper stock were produced in known way.

From the paper samples, made in accordance with the examples and comparative examples, a part was left uncoated, and tested, another part was coated on both sides in known way with polyethylene, and subjected in this form to a testing. Within the framework of the invention, the subsequently cited test methods were taken into account for the evaluation.

Surface Smoothness (a.k.a. Surface Number)

The test took place in on uncoated paper webs, in accordance with the test methods, described in DE 34 26 782 A.

The higher the surface number, the worse the surface quality. Usually, the surface numbers for base papers, made by using photographic celluloses, are - in the case of neutral sizing - in the range from 140 to 190, and when using acid sizing - from 90 to 150.

Edge Penetration of Developer

The paper samples, coated with polyethylene, were cut, and immersed - in the required specimen size - for 14 minutes into a commercially available color

developer bath (T - 30º C). After intermediate washing, treatment with commercially available fixative (fixing solution) and subsequent washing, the specimens were dried, and the depth of penetration (in mm) of the developer solution at the cutting edge was measured with a measuring magnifying glass. The zone of the developer penetration is to be discerned in transmitted light as edge stripes, colored more or less in brownish color. The numerical data in the tables, which follow, are average values of 6 individual measurements, respectively.

Texture Strength

The texture strength (the internal bond strength) was determined in accordance with TAPPI* RC 308 [*TAPPI = Technical Association of the Pulp and Paper Industry] with a Scott Bond Plybond Strength Tester (internal Bond Impact Tester Model B). The numerical values in the tables, which follow, are average values of 5 individual measurements.

Customarily, the values of the texture strength of the base papers, made in conventional way, are - in the case of standard sizing - in the range of 150 to 300 ft.lb/sq.in, and in the case of acid sizing - in the range of 110 to 150 ft.lb/sq.in. The higher the value, the grater the internal bond strength of the paper.

Photochemical Properties

In order for the photochemical properties to be tested, there were taken into

consideration 4 different photographic emulsions, which have different values of the light sensitivity. For example, such an emulsion is described in EP 0023668 A.

To this end, the test emulsion is applied upon the base paper with the help of a casting machine, and dried. The specimen, which has been coated, is illuminated to an average grey shade, developed, and fixed. The assessment (denoted by scores 1 thru 6) takes place visually on the basis of a comparison with a pattern, whereby the score "1" stands for " very good (i.e. outstanding)", and the score 6, denotes "failing score".

The results of all tests thus described are arranged in Tables 3 and 4. As ensues from the Tables, the test results of the base papers, made by using recycled paper stock, are in the range, which is usual for the conventional base papers, produced by using photographic celluloses.

*Tables 3 and 4 follow on the next 2 pages

Table 3 Test results, obtained in Examples 1 thru 3

Example	Surface number	Texture strength Sc. B. (ft.lb/ sq.in)	Edge penetration (mm)	Photochemical Properties Emulsions			
				1	2	3	4
1.1 (1)	180	169	0.18	5	4	2	3
1.2 (1)	189	142	0.21	4	3.5	2	3
1.3 (1)	181	135	0.17	3.5	3.5	2	3
1.4 (1)	167	163	0.22	3	3.5	2	3
1.5 (1)	153	162	0.22	4	3.5	2	3
1.6 (1)	155	165	0.21	4	3.5	2	3
2.1 (1)	155	154	0.22	4	3.5	2	3
2.2 (1)	150	173	0.22	4	3.5	3	3
2.3 (1)	166	175	0.25	4	3.5	3	3
3 (2)	112	120	0.42	4	3.5	3	3

1: BS - climate test (score 1 to 6)
2: Silver chloride test (score 1 to 6)
3: BROVIRA extra-hard (score 1 to 6)
4: LM (score 1 to 6)

1.1 thru 1.6 - Example 1
2.1 thru 2.3 - Example 2

3 - Example 3.
1) neutral sizing
2) acid sizing

Table 4 Test results, obtained in the comparative examples 1 and 2

Example	Surface Number	Texture strength Sc. B. (ft.lb/ sq.in)	Edge penetration (mm)	Photochemical Properties Emulsions*)			
				1	2	3	4
V1 (1)	163	165	0.3	3 - 4	5	3	4
V2 (2)	110	120	0.4 - 0.5	4	4	4	4

* See Table 2

1) neutral sizing
2) acid sizing

Claims:

1. Base paper for photographic emulsion carriers* [*supports], **characterized in that** it consists of a paper core, whose fibrous material contains between 5 and 100% of recycled paper stock (cellulose pulp).

2. Base paper as claimed in claim 1, **characterized in that** besides recycled paper stock, the fibrous material contains a photographic cellulose and/or standard cellulose.

3. Base paper as claimed in claim 1 and 2, **characterized in that** the paper core is treated with a neutral size.

4. Base paper as claimed in claim 1 and 2, **characterized in that** the paper core is treated with an acid size.

5. Base paper as claimed in claim 1 and 2, **characterized in that** the paper core contains a reactive and a non-reactive sizing agent.

6. Base paper as claimed in claim 1 thru 5, **characterized in that** the paper core contains a white pigment.

7. Base paper as claimed in claim 1 thru 6, **characterized in that** the paper core is surface sized.

8. Base paper as claimed in claim 1 thru 7, **characterized in that** the paper core is coated on at least one side with a synthetic resin layer.

9. Base paper as claimed in claim 8, **characterized in that** the synthetic resin layers is hardened by means of irradiation.

10. Base paper as claimed in claim 8, **characterized in that** the synthetic resin layer is a layer, applied by means of extrusion coating.

11. Base paper as claimed in claim 1 thru 7, **characterized in that** the synthetic resin layer is applied as an aqueous dispersion.

12. Base paper as claimed in claim 8 thru 11, **characterized in that** the

synthetic resin layer contains a white pigment.

Translated from the German by John Koytcheff, M. Sc. (Civ. & Water Engrg.);
WHO Postgrad. Fellow (Environm. Engrg.); USNWC/USNC&SC Graduate
The USPTO Translator from German& Germanic languages
US Department of Commerce/USPTO
November 18, 2010